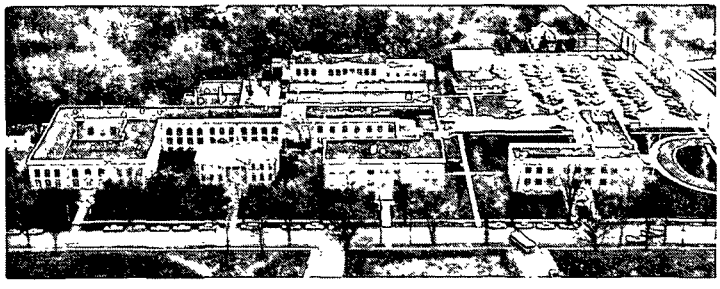

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DETERMINATION OF POLYCHLORINATED BIPHENYLS IN PAPER MILL EFFLUENTS AND PROCESS STREAMS

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INTRODUCTION

Polychlorinated biphenyls (PCB's) are organic compounds which have been sold in the United States as mixtures, called Aroclors. Prior to the spring of 1971, carbonless copy paper contained Aroclor 1242. However, this use was terminated when PCB's were found to possess low-level toxicity. Old carbonless copy paper containing Aroclor 1242 is apparently still entering paper mills using secondary fiber with their raw material, and the PCB's leave the mills in their products, effluents, and sludges.

Regulations designed to minimize the entry of PCB's into the environment via aqueous effluents have been or soon will be promulgated by both federal and state agencies. Consequently, accurate methods for PCB determinations are needed for effluent monitoring and for in-plant use in evaluation of control technology. Although most analysts use similar procedures for determining PCB's, work performed elsewhere has revealed differences amounting to several hundred percent in PCB data on the same paper mill effluents analyzed in different laboratories.

The goal of the current investigation has been to obtain a better understanding of several potential sources of error in determining PCB's in paper mill effluents and process streams within the mill. This information should ultimately lead to better agreement among laboratories.

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Polychlorinated biphenyls, Analytical methods, Chemical analysis, Cellulose fibers, Effluents, Reclaimed fibers, Paper mills, Gas chromatography, Volatilization, Stability, Storage

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ABSTRACT

Special techniques have been found necessary for isolating PCB's from cellulose fiber-containing effluents and process streams and for determining PCB's in effluents from paper mills using recycled fiber. Sources of potential PCB loss from aqueous solutions are revealed and means of avoiding these losses are proposed.

Significant amounts of PCB remained on cellulose fibers following separatory funnel extraction of a fiber-water suspension with hexane or methylene chloride-hexane. Reflux of the fibers with alcoholic KOH was necessary to remove the PCB's. PCB losses due to volatilization from aqueous solution occurred during analysis, but this

was minimized by working in a cool environment and covering the sample with a layer of hexane. The presence of cellulose fibers in PCB-containing effluents enhanced the effluents' stability during storage.

Chromium trioxide oxidation was found to be valuable in cleaning up extracts from paper mill effluents. Perchlorination is apt to yield misleading results.

INTRODUCTION

Polychlorinated biphenyls (PCB's) are commonly determined in industrial effluents by a method involving liquid-liquid extraction, Florisil cleanup, and electron capture gas chromatography, as prescribed by the U.S. Environmental Protection Agency[1]. The utility of this and other methods was evaluated for use on paper mill effluents and process streams within the mill.

ISOLATION OF PCB's FROM FIBER-WATER SUSPENSIONS

Known amounts of Aroclor 1242, 100 µg/l., were added to 1% suspensions of cellulose fibers in water. Incomplete recoveries were experienced when these suspensions were subjected to triple separatory funnel extractions with petroleum ether, hexane, or 15% methylene chloride in hexane. Following the separatory funnel extraction, the fibers were filtered from the sample and the residual PCB was removed from the fibers by reflux in 2% alcoholic KOH, as is normally used for determining PCB's in paperboard.[2] Removal of all residual PCB by the alcoholic KOH was demonstrated by dissolving the fibers in 72% H_2SO_4, diluting with water, and extracting with hexane.

Data in Table 1 resulted from a study designed to determine whether alcoholic KOH reflux of the fibers subsequent to separatory funnel extraction was needed to remove PCB's from fiber-water suspensions with low fiber contents. The results indicate that fibers, even at low concentrations in the sample, retained some PCB's, and that alcoholic KOH reflux was needed for complete PCB removal. However, in analysis of effluents containing less than 0.01% suspended hardwood fibers, the amount of PCB retained by the fibers was small compared with other reported sources of error in PCB determinations (e.g., 20% relative standard deviation for chromatogram quantitation[3]). Somewhat smaller amounts of Aroclor 1242 were retained by softwood fibers.

TABLE 1

Recovery of Aroclor 1242 from Hardwood Fiber Suspensions

Fiber Content, %	Recovery by Extraction, %	Recovery from Fibers, %	Total Recovery, %
0.005	97.0	0.9	97.9
0.01	96.4	2.4	98.8
0.05	91.8	8.4	100.2
0.10	91.8	10.8	102.6
0.16	84.2	9.0	93.2
0.40	80.2	15.8	96.0
0.60	80.0	15.5	95.5
0.80	80.4	15.6	96.0

Thus, it may be concluded that the EPA liquid-liquid extraction technique should be adequate for most effluents containing low amounts of suspended solids and that it is inadequate for fiber-water suspensions within the mill. Because of their high suspended

solids contents, the fiber-water suspensions require a separate alcoholic KOH reflux to remove all of the PCB's from the fibers.

MINIMIZING PCB LOSSES DUE TO VOLATILIZATION

Low recoveries (60-80%) of known amounts of Aroclor 1242 added to aqueous samples were experienced in the summer. Volatilization of PCB's from aqueous solution, as described by Mackay and Wolkoff[4] and Paris, et al.[5], during analysis of the samples seemed to be a possible explanation for the low values. Trapping of the Aroclor 1242 from the gas phase, as shown by the data in Table 2, demonstrated that volatilization could occur from aqueous solutions and fiber-water suspensions. A stream of nitrogen entered through a stopper in the top of a suction flask, impinged upon (but did not bubble through) the sample, and exited via the side arm of the flask into a trap containing deactivated Florisil.[6]

TABLE 2

Volatilization and Trapping of Aroclor 1242

Sample	Start, µg	Remaining, µg	Trapped, µg
Aqueous solution	10	4.0	3.9
Softwood suspension	10	5.8	2.9

Conditions: One hundred ml solution or 0.5% fiber-water suspension in 125-ml suction flask. N_2 flow: 600 ml/min across surface for 2 hours at 23°C. Trap: 0.3 g deactivated Florisil in 5 mm glass tube.

Losses of Aroclor 1242 from fiber-water suspensions in stirred beakers under simulated summer and winter laboratory conditions are shown in Table 3. A comparison of total recoveries from the open, cool (Condition B) and open, warm (Condition D) samples suggests that Aroclor 1242 was lost by volatilization during 5 minutes stirring under summer conditions but not under winter conditions. It may be speculated that PCB loss from the closed, warm beaker (Condition C) occurred because the aluminum foil cover formed an imperfect seal or that some PCB escaped into the air space between the foil and the solution.

TABLE 3

Effect of Temperature and Exposure on PCB Spike Recovery

Conditions[1]	Recovery by Extraction, %	Recovery from Fibers, %	Total Recovery, %
Closed, cool (A)	88.4	11.0	99.4
Open, cool (B)	87.0	13.4	100.4
Closed, warm (C)	76.9	15.2	92.1
Open, warm (D)	73.4	12.2	85.6

[1]One percent hardwood suspension, 57.1 µg/l. Aroclor 1242, 5 minutes stirring with magnetic stirrer. Warm = 30-32°C. Cool = 22-23°C.

These studies have provided the basis for the recommendations listed below for minimizing PCB volatilization losses during sample handling and analysis:

1. Minimize air space in sample container.
2. Keep glassware, hexane, distilled water, and sample below 23°C.

3. Pour hexane into separatory funnel before introducing sample.
4. Maintain layer of hexane on top of aqueous phase.
5. Filter fibers as soon as possible.
6. Avoid pulling air through fibers during filtration.
7. Cook fibers in alcoholic KOH promptly.

Steps 1 through 4 should be of value in isolating PCB's from any aqueous sample. The layer of hexane seals the air-water interface from which volatilization can occur. Steps 5 through 7 are critical if the sample contains suspended fibers from which PCB must be extracted separately. Over half of the Aroclor 1242 has been lost from fibers when they were permitted to air dry before being placed in alcoholic KOH.

SAMPLE STABILITY DURING STORAGE

The need for special extraction procedures to remove PCB's from cellulose fibers suggests that the PCB's are sorbed onto the fibers. Table 2 shows less Aroclor 1242 volatilization from the softwood suspension than from the aqueous solution without fibers. Perhaps sorption of the PCB onto the fibers protected the PCB against volatilization. Sorption would also explain the improved stability of Aroclor 1242 during storage of fiber-water suspensions, compared with aqueous solutions, demonstrated in Figure 1. In that study, the spiking level was 86 µg/l. Aroclor 1242 in river water, and the suspensions contained 1% softwood fibers. Samples were stored in daylight at ambient temperature. Half of the samples contained formaldehyde at 15 ml/l. In a separate investigation, no stability

differences were observed between Aroclor 1242 solutions stored for 10 days in daylight vs. in the dark.

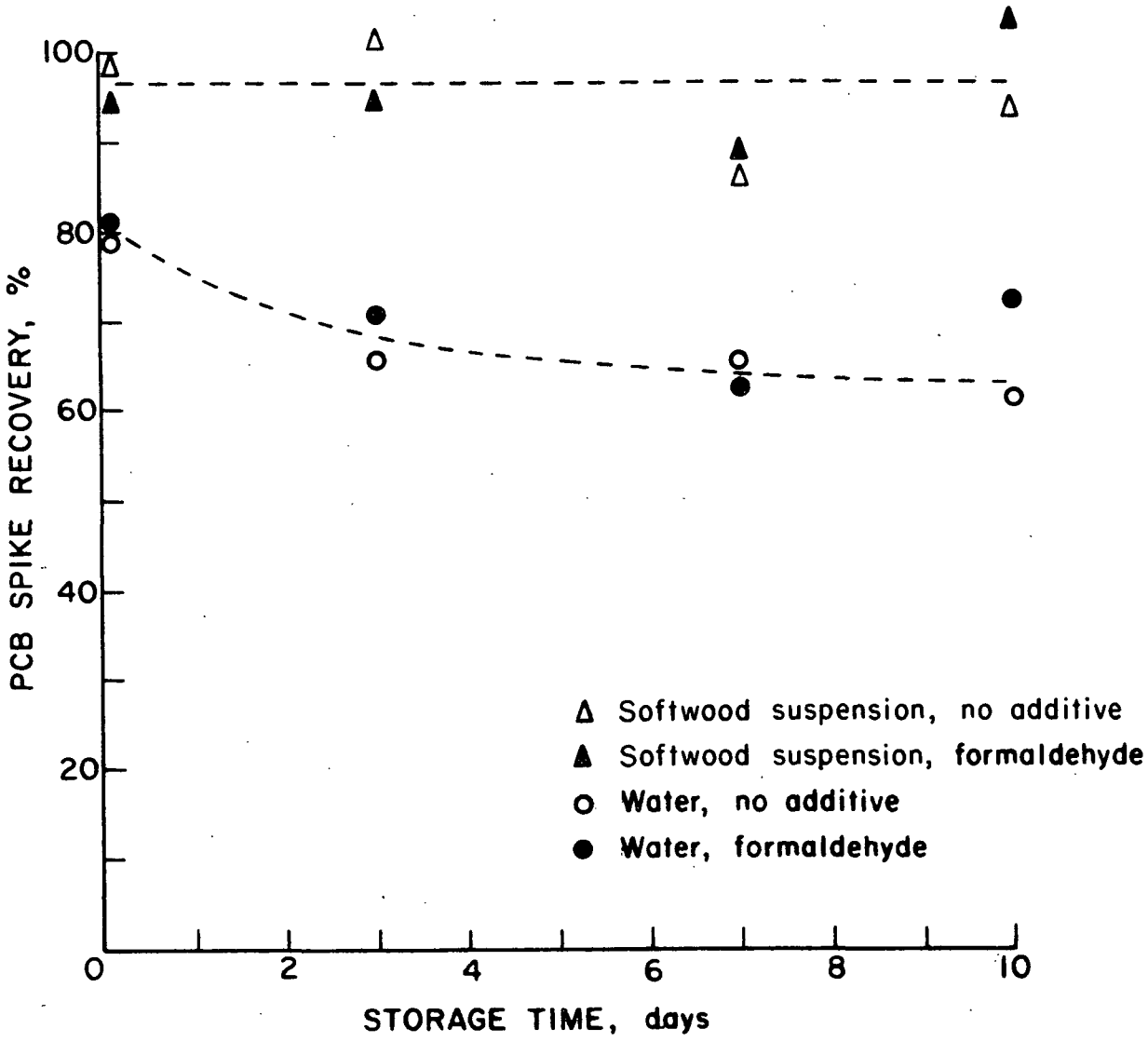

FIG. 1

Stability During Storage of Water and Fiber Suspensions Containing Aroclor 1242

This study did not confirm the finding of Bellar and Lichtenberg that formaldehyde was an effective preservative for PCB's.[7] However, an indirect benefit from adding formaldehyde to industrial effluents and fiber suspensions has been experienced: Formaldehyde inhibits decomposition of non-PCB organics which degrade to liberate sulfur, a common interference on PCB gas chromatograms.

REMOVAL OF INTERFERING PEAKS FROM CHROMATOGRAMS

Perchlorination

Extracts from paper mill effluents should always be cleaned up on a Florisil column prior to gas chromatography. However, it does not remove all interferences. It was hoped, therefore, that the PCB's in paper mill effluents could be perchlorinated to decachlorobiphenyl (DCB), whose long retention time would move it well away from interfering peaks.

The perchlorination procedure used was essentially the method of Huckins, *et al.*[8], modified in order to promote complete perchlorination with minimized volatilization loss of Aroclor 1242. The principal modification consisted of concentrating the extract containing the suspected PCB at room temperature in a culture tube by directing a stream of nitrogen at the top of the tube.

Perchlorination was attempted on authentic effluents from recycling mills as well as on distilled water containing Aroclor 1242 plus other suspected high-boiling components of recycled carbonless copy paper (alkyl biphenyls and alkyl napthalenes). Reaction

mixtures consistently charred, and low DCB yields were obtained on these spiked samples. Aroclor 1242 is thought to occur in paper mill effluents because of the recycling of carbonless copy paper made prior to mid-1971. If pre-1971 carbonless copy paper (with PCB's) is present in a mill's raw material, newer carbonless paper (with alkyl biphenyls, alkyl naphthalenes, or other high-boilers, but not PCB's) is probably also present. Consequently, a mill effluent containing PCB's would quite likely also contain the alkyl biphenyls, alkyl naphthalenes, or other high-boiling compounds. Because these non-PCB components of modern carbonless copy paper reduce the DCB yield, perchlorination of paper mill effluents is apt to give incorrect estimates of the effluents' PCB contents.

Alkyl biphenyls and naphthalenes were also subjected to perchlorination in the absence of PCB. Reaction products were analyzed by FID gas chromatography using temperature programming to improve peak resolution. All samples yielded a peak with the same retention time as DCB. Thus, effluent analysis using perchlorination might incorrectly identify these originally nonchlorinated compounds as PCB's. Consequently, perchlorination is <u>not</u> recommended for determining or confirming PCB's in paper mill effluents.

<u>Mercury and Chromium Trioxide</u>

Interferences due to sulfur may be removed with mercury[1] or, as an alternative, chromium trioxide oxidation[9] followed by a second Florisil cleanup, as shown in Fig. 2. Recoveries of Aroclor 1242 spikes carried through the chromium trioxide treatment have been

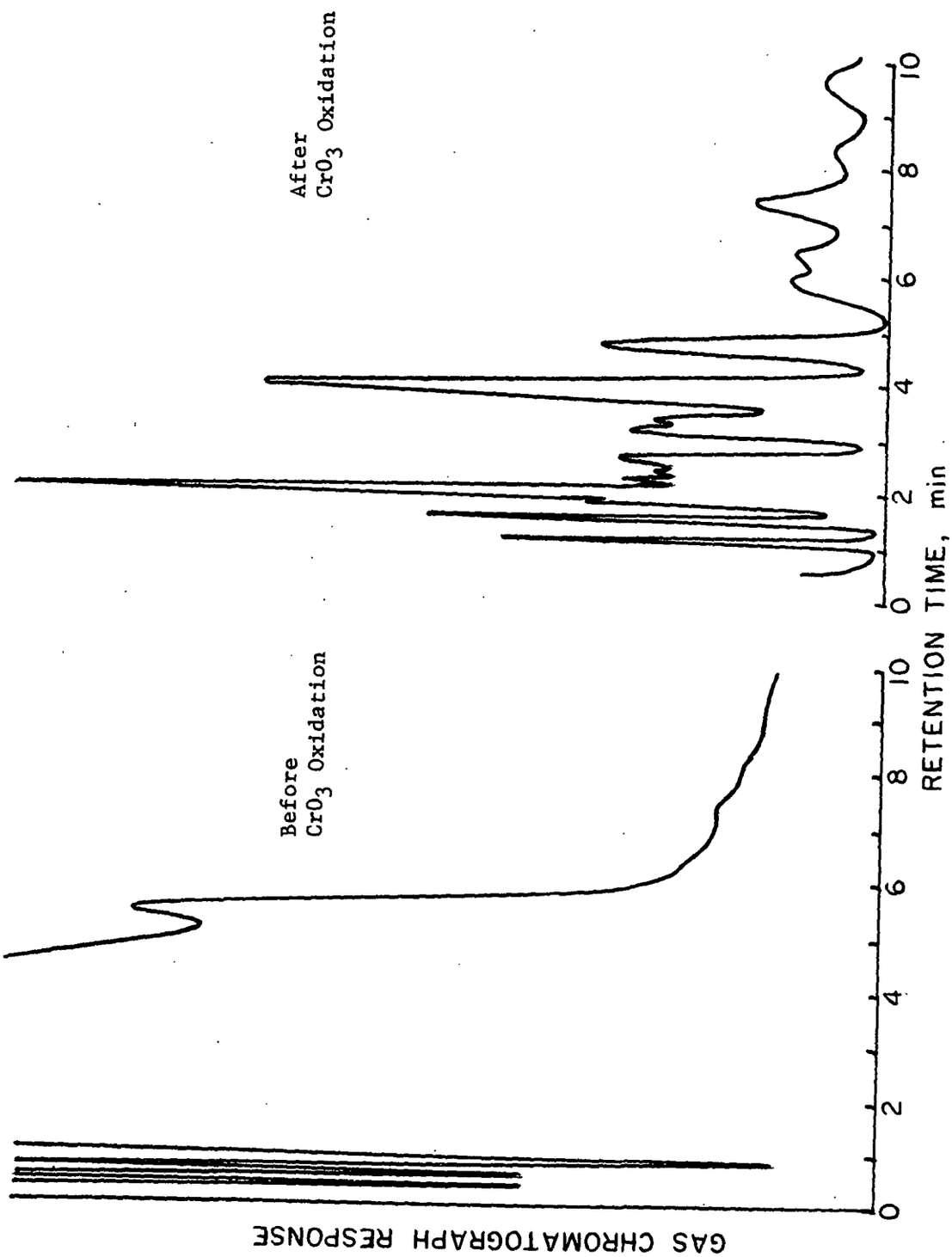

FIG. 2

Pulp Mill Effluent Spiked with Aroclor 1242

approximately 90%. Gentle concentration of the sample extract in the presence of acetic acid is required to prevent loss of the more volatile Aroclor 1242 constituents.

Alkyl naphthalenes, a possible component of newer carbonless copy paper, were removed by the chromium trioxide oxidation, but alkyl biphenyls were not affected. Figure 3 shows the result of using the chromium trioxide oxidation on an extract whose original chromatogram contained large unidentified interferences.

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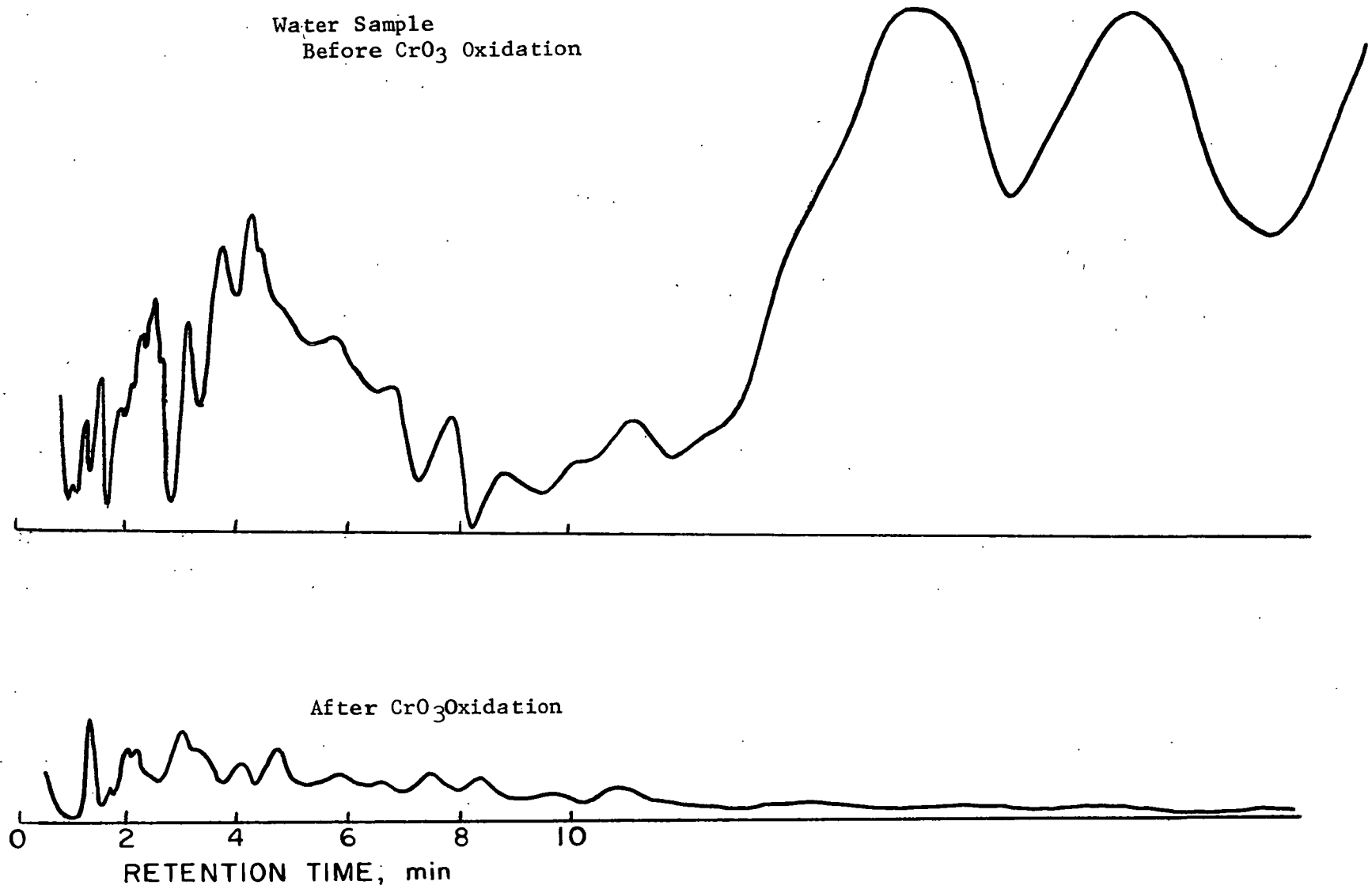

FIG. 3

Effect of Chromium Trioxide Oxidation on Water Sample Containing Interferences